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Quartz crystal microbalance studies have been used to identify anion insertion or cation insertion in polypyrrole films. In the conditions where only a single species is inserted, impedance measurements have been used to characterize the processes of charge injection and diffusion in the films.

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## QCM and Impedance Analysis of Polypyrrole

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Impedance behavior of electroactive polymer films display three distinct regions, characterized by different relaxation times(1,2). At high frequencies, the simultaneous injection of holes (during oxidation of the polymer) and counterion movement (to maintain charge neutrality) is the rate controlling process. At intermediate frequencies, diffusion of holes and ions in the film is rate limiting. At the lowest frequencies, the finite thickness of the film causes the impedance to become purely capacitive (redox capacity region). A schematic of these three regions is shown in fig. 1.

Polypyrrole can be formulated as either an anion-inserting ( $\text{ClO}_4^-$ ) film or as a cation inserting film ( $\text{Na}^+$ ). When polypyrrole is grown (in the oxidized state) by electropolymerization in an electrolyte containing small anions ( $\text{ClO}_4^-$  or  $\text{BF}_4^-$ ), the anions are incorporated into the polymer matrix (doped state). Upon subsequent reduction to the non-conductive neutral state, these anions are released from the film to maintain charge neutrality. Thus, the films are anion-inserting. However, when polypyrrole is grown in an electrolyte solution containing large polymeric anions (poly-4-styrene sulfonate), the incorporated anions are trapped within the polymer matrix(3). Subsequent reduction of the film necessitates the movement of cations into the film to maintain charge neutrality. This is a cation-inserting film (see fig.2).

Analysis of thin films (30-50 mC/cm<sup>2</sup>, about 300-500 Å) by simultaneous Quartz Crystal Microbalance gravimetry and cyclic voltammetry (4), has shown the conditions under which the species being inserted are anions or cations, respectively. The charge data and mass change data agree ideally up to the cyclic voltammetric peak potential. During the latter half of the oxidation scan, some discrepancies have been observed, particularly in the films containing large polymeric anions. The latter region will be discussed as well, to indicate what evidence there is for multiple processes.

Cole-Cole plots for anion-intercalating polypyrrole (PPy/ $\text{ClO}_4^-$ ) show all 3 regions of behavior (5,6)(see fig. 3a). The charge transfer resistance is about 140 Ω at -0.1 V vs SCE (for a 50 mC/cm<sup>2</sup> film in 0.01M  $\text{NaClO}_4$ ).

Polypyrrole grown in larger anions (tosylate (TOS) or poly-4-styrene sulfonate (PSS)) shows no typical diffusion-controlled region for films ranging from 50-500 mC/cm<sup>2</sup> (about 500-4000 Å in thickness)(fig. 3b). The charge transfer resistance for PPy/PSS films is relatively large (about 250 Ω at -0.1 V vs SCE for a 50 mC/cm<sup>2</sup> film in 0.01M NaPSS). The PSS prepared films are less conductive than  $\text{ClO}_4^-$  films and the redox capacity is smaller.

Comparison of diffusion coefficients in the several systems will be made, along with the concentration dependence of each

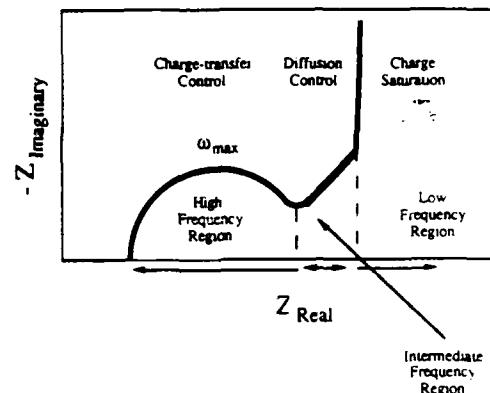


Fig. 1. Generalized Cole-Cole plot for thin-film materials.

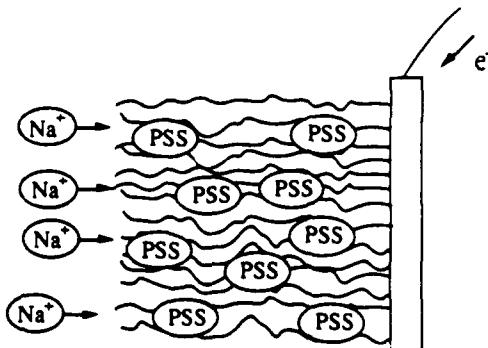


Fig. 2. Schematic of polypyrrole grown in NaPSS, exhibiting cation insertion.

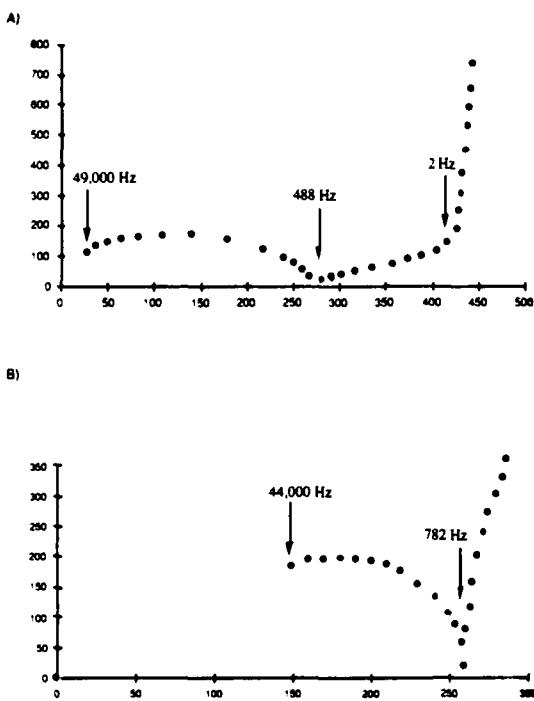


Fig. 3. Cole-Cole plots for (A) PPy in  $\text{LiClO}_4/\text{H}_2\text{O}$  and (B) PPy in  $\text{PSS}/\text{H}_2\text{O}$ .

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